

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

Starch Product of Improved Properties and Method of  
Making the same

We, NATIONAL STARCH PRODUCTS INC., a corporation organized under the laws of the State of Delaware, one of the United States of America, of 270, Madison Avenue, City of New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of starch products of improved properties. More specifically, it relates to the treatment of starches whereby they attain greater viscosity (i.e. water absorptive powers), greater clarity of the cooked pastes, greater resistance to gelling of the pastes upon cooling, and lowered gelatinization point, as compared to the corresponding untreated starch material.

The improved properties set forth above are of particular importance in the manufacture of adhesives, the use of starch as a thickening agent in foods and the fabrication of certain types of textiles and papers. Of particular significance from the standpoint of industrial utilization is the fact that such starches, when cooked in the presence of acids or salts, show markedly less loss of their viscosity and clarity than do the corresponding untreated starches.

It is the prime object of the present invention to produce starch derivatives having the above properties and to devise a method for the ready production of said products. Other objects will become apparent from the ensuing specification.

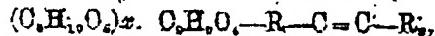
In this specification the term "starch" includes starch from any source, such as corn, wheat, potato, tapioca, waxy maize.

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sago, sweet potato and the like, and also starches which have been converted, either by acid hydrolysis, oxidation or by other means.

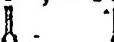
We have discovered that starch derivatives of these and other improved properties of commercial importance may be formed by the production of un-gelatinized starch derivatives containing sulfonic acid groups. This production can be effected either by reacting raw starch with suitable reagents or by reacting certain unsaturated, ungelatinized starch derivatives with a chemical containing the sulfonic acid group, such as a bisulfite. In either event, the improved un-gelatinized starch derivative of the present invention is characterized by containing a sulfonic acid group.

When unsaturated ungelatinized starch derivatives are employed, the starch unsaturation is caused by an ethylenic double bond as shown diagrammatically by the following formula:



$R_1, R_2$

wherein  $R_1$  may be  $-OC-$ ,  $-OCCH_3-$ ,



$-OOH$ ; or  $-OCH_2O^-$ , and wherein, if both  $R_1$  and  $R_2$  are hydrogen,  $R_1$  must be a member of the first group consisting of formyl, cyano, carboxy, carbalkoxy and carbalkyl radicals; and if either  $R_1$  or  $R_2$  or both are members of the second group

consisting of formyl, cyano, carboxy, alkyl, aryl and substituted alkyl and aryl radicals, then  $R_1$  must be hydrogen or a member of the second group. An

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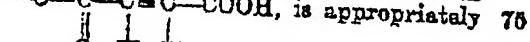
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- example of the first type of derivative in which both R<sub>1</sub> and R<sub>2</sub> are hydrogen is the tapioca starch ester of itaconic acid (see Example VIII).
- An example of the type of derivative in which both R<sub>1</sub> and R<sub>2</sub> are not hydrogen is the potato starch ester of citraconic acid (see Example III). Examples of the type of derivative in which only one of the radicals R<sub>1</sub> and R<sub>2</sub> are not hydrogen are the corn starch ester of malic acid in which either R<sub>1</sub> or R<sub>2</sub> is a carboxy radical (see Example I) and the tapioca starch ester of crotonic acid in which either R<sub>1</sub> or R<sub>2</sub> is an alkyl radical (see Example II). In all of these examples, in which either R<sub>1</sub> or R<sub>2</sub> or both are not hydrogen, R<sub>1</sub> is hydrogen, but this is not essential to the carrying out of the invention. To put the matter in another way, if R<sub>1</sub> is not one of the radicals of the first group, but instead may be hydrogen, then either R<sub>1</sub> or R<sub>2</sub> or both must be a member of the second group.
- It will be noted that we have excluded that type of unsaturated derivative in which R<sub>1</sub> and R<sub>2</sub> are hydrogen and R<sub>3</sub> is not a radical chosen from the first group. We have found that the use of this latter type of unsaturated derivative produces a completely different type of product from that of the present invention.
- Various derivatives of starch may be reacted with bisulfite for the purposes of this invention. Among the suitable starch derivatives into which sulfonic acid groups may be introduced are, for example, certain of the starch esters prepared by treating starch in aqueous sus-
- sension with alkali and with anhydrides of organic acids containing double bonds, such as the anhydrides of maleic, citraconic, itaconic and crotonic acids. It is to be understood, however, that the practice of the invention is not limited to starch derivatives made by any particular method, the only limiting factor being that the starch derivatives treated must contain unsaturated radicals of the type described, the unsaturation being due to the presence of an ethylenic double bond.
- The treatment of unsaturated starch derivatives with bisulfite, according to our invention, can be carried out in aqueous suspension, at temperatures below the gelatinization temperature of the starch or starch derivative. This makes it possible to filter and wash the resultant starch product—a fact of considerable importance in the industrial application of this process.
- Although in dealing with complex reactions of the type under discussion, analysis of the molecular changes involved cannot be carried out with

absolute precision, it is believed that the action of the bisulfite such as sodium bisulfite on the unsaturated starch derivative causes a saturation of the derivative by the attachment of the bisulfite group to one of the unsaturated carbon atoms on the chain. Thus, if the corn starch ester of maleic acid, which has the general form starch



reacted with sodium bisulfite, the resultant starch derivative will, it is believed, exhibit the molecular structure starch-



While the



sulfonic acid group is here illustrated as being attached to the alpha carbon of the free carboxyl group, it might instead be attached to the beta carbon of the free carboxyl group.

It should be noted that the various unsaturated starch derivatives which we employ have been so treated that the granule structure of the starch has not been destroyed, and the substitution of the hydroxyl groups has probably taken place on the surface of the granule. According to the process of the present invention, the unbroken granule of the starch is retained; in other words, the addition of the sulfonic acid groups probably takes place with unsaturated groups on the surface of the granule, and again, there is, therefore, a relatively low degree of substitution.

Although, as stated above, the bisulfite addition can take place in aqueous suspension, it has been found that the addition of the sulfonic acid group to the unsaturated radical also takes place readily if the unsaturated starch derivative is refluxed in ethanol or other non-aqueous media, in the presence of bisulfite. This is especially true of the treatment of the itaconic acid ester of starch with bisulfite. It is understood, of course, that starch will not gelatinize in the absence of substantial proportions of water, and therefore, this alcohol-refluxing method has the same advantages as the aqueous method, namely, it results in an ungelatinized, washable, filterable product.

As has already been set forth, it is possible to form an ungelatinized starch granule containing sulfonic acid groups, which granule corresponds to the molecular structure previously set forth; by utilizing raw starch (that is, starch which does not contain the unsaturated radicals). This ungelatinized raw starch is treated with alkali and with

a compound of the groups specified which contains both a sulfonic acid group and a group capable of reacting with the hydroxyl groups in the starch to produce starch ethers or esters. The said compounds, which combine the functions of ether-formation and sulfonic acid addition are chloromethyloisethionic acid ( $\text{CH}_2\text{Cl}-\text{CH}_2-\text{SO}_3\text{H}$ )  
benzyl chloride para-sulfonic acid



5.  $\beta$ -unsaturated olefins sulfonic acids such as ethene sulfonic acid ( $\text{CH}_2=\text{CHSO}_3\text{H}$ ), and salts of said acids. Thus, there results an ether or ester derivative of starch which contains sulfonic acid groups. In order to cause substantial reaction of these acids with starch, it has been found that rather high concentrations of alkali are ordinarily advisable. It has already been explained that gelatinization of the starch is to be avoided, and since this high alkali content would ordinarily cause gelatinization of the starch granules, it is advisable to suspend the starch in a concentrated sodium sulfate solution before addition of the alkali and the subsequent addition of the ether or ester-forming derivative. The sodium sulfate prevents gelatinization of the starch in the presence of the high alkali concentrations needed for this reaction. This anti-gelatinization effect is apparent even at temperatures up to 100° C. Of course, it is possible to use lower quantities of alkali so as to avoid gelatinization, making unnecessary the use of sodium sulfate, but a considerably lower degree of substitution results.
40. It will be seen that we have indicated here the production of two types of starch derivatives containing sulfonic acid groups, i.e. starch esters and starch ethers. As compared to the starch esters, starch ethers and raw starch from which they are produced, the products of the invention are altered in the following respects:
50. 1. They have increased water absorption. That is, they may be cooked with a larger quantity of water than the raw starch or the untreated starch ester or ether to produce a paste of a given viscosity.
55. 2. The cooked suspensions, or pastes, are clearer and more translucent.
3. The cooked suspensions, or pastes, exhibit a lessened tendency to set to a gel upon cooling.
60. 4. The gelatinization temperature is lower.

5. The clarity and viscosity of the cooked starch pastes are less sensitive to the presence of acids and salts; that is, they do not lose clarity and thin out in the presence of acids and salts to the extent that starch derivatives containing only carboxyl groups would do.

When we refer to treatment with bisulphite, it is understood that we mean sodium, potassium or ammonium bisulfite or any other acid salt of sulfurous acid.

The degree of improvement brought about by the process of the invention depends upon the following variables:

1. The proportion of unsaturated radicals in the starch to be treated with bisulfite. The greater the proportion of unsaturated radicals present in the starch, the greater the amount of sulfonic acid groups which may thus be introduced into the starch. Excellent results have been obtained using starches containing from 1 unsaturated radical per 140 anhydroglucose units up to 1 unsaturated radical per 16 anhydroglucose units. In those cases where one reacts raw starch with a compound containing both a sulfonic acid group and a group capable of reacting with the hydroxyl groups in the starch to produce starch ethers, roughly the same range applies, namely, the introduction of from 1 sulfonic group per 140 anhydroglucose units in the starch to 1 sulfonic group per 16 anhydroglucose units.

2. The proportion of bisulfite used, based on the unsaturated radicals in the starch. At room temperature, with about 100 a four hour period of treatment, we prefer to use an amount of bisulfite equal to seven-fold the stoichiometrical amount calculated upon the weight of the unsaturated radical. At higher temperatures, say at 50° C., an equivalent result is obtained by using only about four times the stoichiometrical amount required by the weight of the unsaturated radical in the starch. On the other hand, far lower amounts of bisulfite can be used but with proportionately lesser degree of substitution.

3. The period of treatment. A longer period of treatment permits decreased temperature and/or decreased amount of bisulfite.

4. Temperature. The temperature of the reaction affects the other variables. At higher temperatures, the other variables may be decreased. As is common with many chemical reactions, the factors of the quantity of reagent, temperature and period of reaction are interrelated, i.e., the temperature is inversely proportional to the amount of reagent and the period.

of reaction is inversely proportional to the temperature and amount of reagent. Referring to increased temperatures, it should be remembered that at temperatures above 50° C. there will be the problem, in aqueous media, of gelatinization of the starch; this, however, can be overcome by carrying out the reaction in a saturated sodium sulfate solution, as previously described.

The following examples will further illustrate the embodiment of the invention.

#### EXAMPLE I.

15 This example illustrates the treatment of a corn starch ester of maleic acid with sodium bisulfite.

100 parts of corn starch ester of maleic acid (starch —O—O—CH=CHCOOH)



20 containing 1 maleic acid ester radical per 28 anhydroglucose units is suspended in 200 parts of water in which is dissolved 15 parts of sodium bisulfite. The mixture is stirred for 4 hours at room temperature.

25 The starch product is then filtered and washed. The resultant product has the improved properties previously described, namely, increased water absorption, greater clarity, lessened tendency of the 30 cooked paste to gel upon cooling, lowered gelatinization temperature, and less sensitivity to acids and salts—all as compared to the starch ester prior to introduction of the sulfoxide acid groups.

#### EXAMPLE II.

This example illustrates the treatment of a tapioca starch ester of crotonic acid with potassium bisulfite.

100 parts of tapioca starch ester of 40 crotonic acid.

(starch —O—C—CH=CH—CH<sub>3</sub>)



containing 1 crotonic ester radical per 26 anhydroglucose units is suspended in 200 parts of water in which is dissolved 8 parts of potassium bisulfite. The suspension of starch is stirred for three hours, maintaining the temperature at 50° C. The starch is then filtered and washed. The resultant product exhibits the improved properties described in Example

#### EXAMPLE III.

This example illustrates the treatment of potato starch ester of citraconic acid 55 with ammonium bisulfite.

100 parts of potato starch ester of citraconic acid

CH<sub>3</sub>

(starch —O—C—CH=C—COOH)



containing 1 citraconic acid ester radical per 19 hydroglucose units is suspended in 200 parts of water in which is dissolved 25 parts of ammonium bisulfite. After stirring the suspension for 6 hours at room temperature, the starch is filtered and washed. The improved properties described in Example I are also noted in this product.

#### EXAMPLE IV.

This example illustrates the treatment of a corn starch ether of 1-hydroxy 3-carboxy propene-2,3 with sodium bisulfite.

100 parts of the corn starch ether derivative containing the ether radical of 1-hydroxy 3-carboxy propene-2,3 (starch —O—CH<sub>2</sub>CH=CH—COOH) in the proportion of 1 radical per 62 anhydroglucose units is suspended in 200 grams of water in which is dissolved 20 grams of sodium bisulfite. The mixture is stirred for 4 hours at room temperature. The starch is then filtered and washed, resulting in the improved product previously described.

#### EXAMPLE V.

This example illustrates the treatment of an unmodified starch wherein the unmodified starch is reacted with a compound which contains the sulfonic group.

100 parts of unmodified corn starch is suspended in 200 parts of water in which has been dissolved 3.5 parts of caustic soda and 75 parts of sodium sulfate. There is then added 5.0 parts of sodium benzyl chloride para sulfonate. The mixture is stirred and heated at 60° C. for 4 hours. The alkali is then neutralized with acid and the starch is filtered and washed, resulting in the improved product previously described.

#### EXAMPLE VI.

This example, like the previous one, illustrates the treatment of an unmodified starch.

100 parts of unmodified corn starch is suspended in 200 parts of water in which has been dissolved 4.5 parts of sodium hydroxide and 75 parts of sodium sulfate. There is then added 5 parts of sodium chloro-methyo-isethionate

100

(Cl—CH<sub>2</sub>CH(OH)—CH<sub>2</sub>SO<sub>3</sub>Na).

The mixture is stirred at room temperature for 17 hours. The alkali is then neutralized with acid and the starch filtered and washed. This product also exhibits the improved properties previously noted.

#### EXAMPLE VII.

This example illustrates the treatment of a corn starch ester of maleic acid with 120 sodium bisulfite. It differs from Example I in that a starch derivative is used which

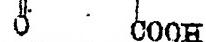
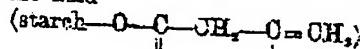
contains a greater proportion of maleic acid ester radicals and uses a larger proportion of bisulfite.

- 100 parts of corn starch ester of maleic acid containing 1 maleic acid ester radical per 15 anhydroglucose units is suspended in 200 parts of water in which is dissolved 25 parts of sodium bisulfite and 75 parts of sodium sulfate. The mixture is stirred 10 for 4 hours, maintaining the temperature at 75° C. The starch is then filtered and washed. The sodium sulfate is used in this example because the elevated temperature would otherwise cause gelatinization of the starch.

#### EXAMPLE VIII.

This example illustrates the treatment of a starch derivative with bisulfite-alcohol suspension rather than in an aqueous medium.

100 parts of tapioca starch ester of itaconic acid



containing 1 itaconic ester radical per 26 anhydroglucose units is suspended in 300 parts of ethyl alcohol containing dispersed therein five parts of sodium bisulfite. The mixture is refluxed for 4 hours. The starch product is then filtered and washed

- 30 in the usual manner, exhibiting the improved properties previously described.

Methods have previously been proposed whereby ungelatinized starches are treated in water suspension with alkali and certain organic acid anhydrides at a pH within the range 7 to 11. The improved properties of the starch so treated, as compared to the raw, untreated starch, are similar, although to a lesser degree, to the improved qualities obtained in the present process. In other words, the starch esters produced by the organic acid anhydride treatment exhibit the properties of increased water absorption, greater clarity, and stability, as compared to the untreated starch. The starch products now produced by the present method of introducing sulfonic groups into the starch molecule exhibit a further improvement in these same qualities of water absorption, clarity, and stability, as previously described.

In the organic acid anhydride treatment the effect of the organic acid anhydrides upon the starch properties has been attributed to the fact that starch ester derivatives were formed, in which one carboxyl group of the dicarboxylic acid anhydride was esterified with a hydroxyl group of the starch molecule, whereas one carboxyl group remained unesterified. This free, or unesterified, carboxyl group or its alkali metal salt is

believed to have a very great affinity for water, thus accounting for the fact that 65 the starches so treated absorb greater quantities of water when cooked, and exhibit greater clarity, as compared to the untreated starches. It has also been suggested that the esters formed with the 70 hydroxyl groups in the amylose, or linear fraction of the starch, could be considered as taking the form of side groups or branches, thus preventing the linear or amylose molecules from becoming 75 oriented in a closely parallel fashion with each other and with the linear portions of the amylopectin or branched molecule fraction of the starch, and thereby resulting in the prevention of association of 80 the starch molecules through hydrogen bonding between the hydroxyl groups. In this manner the retrogradation or setting of the starch to a gel is prevented.

With reference to the present invention 85 wherein sulfonic acid groups are introduced into the starch molecule, it is believed that the further improved properties are due to the fact that sulfonic acid groups are, in general, more 90 acidic (that is, more highly dissociated) than carboxylic acid groups and, in consequence, have even greater affinity for water than do the carboxyl groups.

The characteristics of high water 95 absorption, greater clarity and greater resistance to gelling as well as lowered gelatinization temperature point to obvious commercial and industrial uses for the product of our invention. It is of 100 value in adhesives and also as a thickening agent in foods and other manufactures. Also of particular significance to the food industry is the resistance of the product of the invention to break 105 down upon cooking in the presence of acids or salts. The manufacture of food preparations such as salad dressings, pie fillings, and the like frequently involves cooking of starch or starch derivatives in 110 the presence of acids and/or salts and, as stated, the starch of our invention shows substantially less tendency to loss of viscosity and clarity under such conditions, as compared to the corresponding 115 untreated starches. It is, of course, understood that before using any particular starch derivative in foods, its non-toxicity must first be investigated and fully established.

These same improved qualities give the products of our invention great value in textile and paper fabrication. In this connection, it is noted that the sulfonic acid group increases the affinity of the starch 125 toward cellulose; an important characteristic when the product is used in wash-resistant sizes and finishes for

textiles. For the same reason, it is adaptable to the manufacture of paper beater sizes because of the increased retention of the starch in the paper fibres. The characteristic of lowered gelatinization temperatures is of particular interest in the preparation of laundry starches since it permits the preparation of starches requiring lower temperatures for cooking and shorter cooking times.

What we claim is:-

1. The method of forming an ungelatinized starch derivative having improved water absorptive powers and a lowered gelatinization point which comprises either reacting a member of the group consisting of chloromethyleisethionic acid and salts thereof,  $\beta$ -unsaturated olefins sulfonic acids and salts thereof, and benzyl chlorides para-sulfonic acid and salts thereof with raw starch in the presence of alkali under conditions as herein defined for avoiding gelatinization, or reacting, under the said conditions, a member of the group consisting of sulphydric acid and the acid salts thereof with an unsaturated starch derivative having an ethylenic double bond of the form  $(C_6H_{10}O_5)_x C_6H_9O_4 - R - C = C - R_1$ , in

30 which  $R$  is a member of the group consisting of  $-OC-$ ,  $-OCCH-$ ,  $-COH-$ ,



or  $-OCH_2O-$ , and in which, if both  $R_1$  and  $R_2$  are hydrogen,  $R$  must be a member of the first group consisting of formyl, cyano, carboxy, carbalkoxy and carbalkyl radicals and in which, if either  $R_1$  or  $R_2$ , or both are members of the second group consisting of formyl, cyano, carboxy, alkyl, aryl and substituted alkyl and aryl radicals, then  $R_1$  must be hydrogen or a member of the second group.

2. The method of claim 1, wherein raw

starch is reacted with sodium chloromethyleisethionate.

3. The method of claim 1, wherein raw starch is reacted with sodium benzyl chloride parasulfonate.

4. The method of claim 1, wherein raw starch is reacted with ethane sulfonic acid.

5. The method of claim 1 in which the starch derivative is an unsaturated starch ester.

6. The method of claim 1 in which the starch derivative is an unsaturated starch ether.

7. The method of claim 1 wherein the unsaturated starch derivative is reacted with sodium bisulfite.

8. The method of claim 1 wherein the unsaturated starch derivative is reacted with potassium bisulfite.

9. The method of claim 1 wherein the unsaturated starch derivative is reacted with ammonium bisulfite.

10. The method of claim 1 wherein the starch derivative is held in aqueous suspension during the reaction.

11. The method of claim 1 wherein the starch derivative is held in no-aqueous suspension during the reaction.

12. The method of claim 1 in which the unsaturated starch derivative is reacted in a medium of ethyl alcohol.

13. An ungelatinized starch derivative comprising the reaction product of the method claims 1-12.

14. The method of making an ungelatinized starch derivative having improved absorbent powers and a lowered gelatinization point, and the product thereof, substantially as hereinbefore described.

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